AD-A254 852

②

HOW TO MAKE WATER RUN UPHILL

Manoj K. Chaudhury and George M. Whitesides

Dow Corning Corporation
Midland, MI 48686
and
Department of Chemistry
Harvard University
Cambridge, MA 02138

S DTIC ELECTE SEP 0 3 1992 D A

Technical Report No. 48 (July 1992)

Interim Technical Report
(Accepted for publication in Science)

The views and conclusions in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the U.S. Government.

92 9 02 276

92-24568

REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	Approved for public release; distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 48	5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION Harvard University	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION DARPA

6c. ADDRESS (City, State, and ZIP Code) Office for Sponsored Research Holyoke Center, Fourth Floor Cambridge MA 02138-4993	7b. ADDRESS (City, State, and ZIP Code) 1400 Wilson Boulevard Arlington VA 22209-2308

8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS (City, State, and ZIP Code) Chemistry Division, Code 1113 Office of Naval Research Arlington VA 22217-5000	10. SOURCE OF FUNDING NUMBERS			

	PROGRAM ELEMENT NO. 86-K-0756	PROJECT NO.	TASK NO. a400011dd2	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)

"How to Make Water Run Uphill"

12. PERSONAL AUTHOR(S)
M.K. Chaudhury and G.M. Whitesides

13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) July 1992	15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A surface having a spacial gradient in its surface free energy was capable of causing drops of water placed on it to move uphill. This motion was the result of an imbalance in the forces due to surface tension acting on the liquid-solid contact line on the two opposite sides ("uphill" or "downhill") of the drop. The required gradient in surface free energy was generated on the surface of a polished silicon wafer by exposing it to the diffusing front of a vapor of

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Harold Guard	22b. TELEPHONE (Include Area Code) 202/696-4409	22c. OFFICE SYMBOL

DD Form 1473, JUN 86   Previous editions are obsolete.   SECURITY CLASSIFICATION OF THIS PAGE

decyltrichlorosilane, $Cl_3Si(CH_2)_9CH_3$. The resulting surface displayed a gradient of hydrophobicity (with the contact angle of water changing from 97° to 25°) over a distance of 1 centimeter. When the wafer was tilted from the horizontal plane by 15°, with the hydrophobic end lower than the hydrophilic, and a drop of water (1 to 2 microliters) was placed at the hydrophobic end, the drop moved toward the hydrophilic end with an average velocity of about 1 to 2 mm/sec. In order for the drop to move, the hysteresis in contact angle on the surface had to be low ($\leq 10°$).

How to Make Water Run Uphill

Manoj K. Chaudhury* and George M. Whitesides*

M. K. Chaudhury,
Dow Corning Corporation,
Midland, MI   48686.

G. M. Whitesides,
Department of Chemistry,
Harvard University,
Cambridge, MA   02138.

A surface having a spacial gradient in its surface free energy was capable of causing drops of water placed on it to move uphill. This motion was the result of an imbalance in the forces due to surface tension acting on the liquid-solid contact line on the two opposite sides ("uphill" or "downhill") of the drop. The required gradient in surface free energy was generated on the surface of a polished silicon wafer by exposing it to the diffusing front of a vapor of decyltrichlorosilane, $Cl_3Si(CH_2)_9CH_3$. The resulting surface displayed a gradient of hydrophobicity (with the contact angle of water changing from 97° to 25°) over a distance of 1 centimeter. When the wafer was tilted from the horizontal plane by 15°, with the hydrophobic end lower than the hydrophilic, and a drop of water (1 to 2 microliters) was placed at the hydrophobic end, the drop moved toward the hydrophilic end with an average velocity of about 1 to 2 mm/sec. In order for the drop to move, the hysteresis in contact angle on the surface had to be low (≤10°).

The motion of liquid drops on surfaces, induced by thermal gradients, has been observed experimentally and discussed theoretically (1-4). This type of drop motion is a consequence of the Marangoni flow within the drop that is set up by thermal gradients. Motion of liquid driven by Marangoni flow is also evident in the classical "tear of wine" effect (5). Evaporation of alcohol from the liquid-solid meniscus creates a local rise of the surface tension in the liquid, which induces a surface flow (and in turn a bulk flow) of wine on the wall of the wine glass; the accumulating liquids return in the form of drops. Cottington et al. reported that drops of several oils moved freely on a stainless-steel surface when the oils contained certain types of surfactant additives (6). The authors postulated that the nonuniform evaporation of the surfactant resulted in a surface tension gradient in the liquid drop; this gradient caused the drops to move. This motion appears to be another example of the Marangoni effect.

We report a new type of drop motion that is induced entirely by a surface chemical gradient of a solid substrate. What distinguishes the motion described here from those reported earlier (1,2,4-6) is the fact that no Marangoni forces act on the liquid--instead, the motion results from the imbalance of the surface tension forces acting on the two opposite sides of the drop edge. Figure 1 represents a cross section of a water drop placed on a surface that has a spatial gradient in the surface free energy. The unbalanced Young's force (dF_Y) experienced by this section of the drop is given by Eq. 1.

$$dF_Y = [(\gamma_{SV} - \gamma_{SL})_A - (\gamma_{SV} - \gamma_{SL})_B]dx \qquad (1)$$

Here, γ_{SV} and γ_{SL} are the surface free energies of the solid-vapor and solid-

liquid interfaces, and dx is the thickness of the section of the drop. If θ_A and θ_B represent the local contact angles at points A and B, then Eq. 1 can be represented as

$$dF_Y = \gamma_{LV}(\cos \theta_A - \cos \theta_B)dx \qquad (2)$$

The surface free energy of the liquid-vapor interface is γ_{LV}. The net force (F_Y) experienced by the drop can be obtained by integrating Eq. 2 over the entire width of the drop. If the contact angle at point A is smaller than that at point B, the drop will move in the direction of higher γ_{SV}. This motion has two effects: it decreases the area of vapor-solid interface having the larger interfacial free energy while increasing that having lower free energy, and it increases the total area of solid-liquid interface. Both changes in free energy, effected over a distance, constitute a force driving the drop uphill, against the force of gravity. For a surface that exhibits high hysteresis in contact angles, however, the receding contact angle at point B may become smaller than the advancing contact angle at point A. Under this condition, the drop will not move (3.7). The presence of a gradient in surface tension is thus not, by itself, sufficient to ensure motion of liquid drops--the surface must also have low hysteresis in contact angles and be free of defects that pin the edge of the drop (8).

The method we used to produce gradients in chemical compositions and surface tension on solid surfaces is a modification of the method developed first by Elwing et al. (9). It is based on allowing the surface of a silicon wafer to react with vapors of a volatile alkylchlorosilane by using a diffusion controlled process. The silanization reactions reported by Elwing et al. were

carried out in solvents and exhibited large hysteresis in contact angles (20°

to 40°) (10). Our work used a method that generates gradient surfaces of lower

hysteresis (6° to 8°). This combination of gradient and hysteresis caused 1 to

2 μl drops of water to move up a 15° slope along the direction of increasing

surface free energy, with average velocities of 1 to 2 mm/s (11).

The gradient surface was prepared by allowing the vapor of

decyltrichlorosilane ($Cl_3Si(CH_2)_9CH_3$, $RSiCl_3$) to diffuse over a silicon wafer

(Fig. 2). A clean (12) silicon wafer was placed at a distance of 2 mm from a

solution of $RSiCl_3$ in paraffin oil. As the silane evaporated and diffused in

the vapor phase, it generated a gradient of concentration decreasing along the

length of the wafer. The profile of this gradient was imprinted onto the

silicon wafer by reaction with its surface. The edge of the wafer closest to

the silane became hydrophobic; the farthest end remained hydrophilic. The

steepness of the gradient was a function of the time of exposure of the wafer

to the vapor of the silane. After the formation of the chemical gradient, the

wafer was placed in warm distilled water (65 °C) for 1 min, rinsed thoroughly

in running distilled water, and stored in distilled water at room temperature

(13).

The gradient surfaces were characterized with contact angle measurements

and ellipsometry. The typical wettability gradient produced by exposing the

wafer to vapors of $RSiCl_3$ for 5 min is shown in Fig. 2. The contact angles

decreased smoothly (14); the hysteresis of contact angles was about 10° on the

hydrophobic edge of the wafer and 6° to 8° for most of the gradient, but

increased abruptly at the hydrophilic end. The thickness of the alkylsiloxane

layer, obtained by ellipsometry, was about 6 Å (15) at the hydrophobic end of

the gradient. This value indicates that the layer is significantly less than a

monolayer and is disordered (16). The thickness decreased steadily at a rate
of about 1 Å/mm up to a distance of 5 mm from the hydrophobic edge, beyond
which the estimation of thickness by ellipsometry became unreliable.
Measurements of contact angles indicated that a gradient was present up to a
distance of 1 cm from the hydrophobic edge.

The motion of water drops was examined by placing them on the hydrophobic
edge of the gradient surface. The uphill motion of a water drop on a gradient
surface that was inclined by 15° from the horizontal plane is shown in Fig. 3.
The speeds of the drops varied across the gradient and with the size of the
drop; average speeds of 1 to 2 mm/s were observed for 1 to 2 μl drops on the
steeper part of the gradient (17). The shape of the drop shown in Fig. 3 is
that of a spherical cap. The difference of the contact angles in the advancing
and receding edges of the drop was only about 2° to 3°. The effect of gravity
on the drop shape was not significant here because the radius of the drop (1 to
1.5 mm) was smaller than the Laplace length (2.7 mm) (18). The near-spherical
shape of the drop appears to be a consequence of the equilibration of the
Laplace pressure inside the drop, which is consistent with the model proposed
by Brochard (3).

Water was not the only liquid that moved across such gradient surfaces;
other liquids such as glycerol and chloroform also moved. The motion of these
liquids was, however, examined by keeping the gradient surface horizontal.

Although we have not studied these factors in any detail, the speeds of
the liquid drops depended on hysteresis in contact angles, surface tension and
viscosity of the drops, drop volume, the steepness of the gradient, and the
inclination of the gradient surface. Detailed understanding of the kinetics of
drop motion on gradient surfaces should take these factors into account. The

gradient surfaces reported here are easily prepared. They should be useful in studying the motion of liquid drops induced by chemical gradients, and the interplay of chemical and thermal gradients.

Notes and References

1. H. Bouasse, Capillarité et Phénomènes Superficielles (Delagrave, Paris, 1924).
2. N. O. Young, J. S. Goldstein, M. J. Block, J. Fluid Mech. 6, 350 (1959).
3. F. Brochard, Langmuir 5, 432 (1989).
4. K. D. Barton and R. S. Subramanian, J. Colloid Interface Sci. 133, 211 (1989).
5. A. W. Adamson, Physical Chemistry of Surfaces (Wiley, New York, ed. 3, 1976).
6. R. L. Cottington, C. M. Murphy, C. R. Singleterry, Adv. Chem. Ser. 43, 341 (1964).
7. E. Raphael, C. R. Acad. Sci. Paris II 306, 751 (1988).
8. T. Ondarcuhu and M. Veyssie, J. Phys. II 1, 75 (1991).
9. H. Elwing, S. Welin, A. Askendal, U. Nilsson, I. Lundstrom, J. Colloid Interface Sci. 119, 203 (1987).
10. C.-G. Golander, Y.-S. Lin, V. Hlady, J. D. Andrade, Colloids Surf. 49, 289 (1990).
11. These values of speed are approximate and variable. The effects of drop volumes on speeds have not been rigorously examined. Qualitatively, it was observed that the speeds increased as the volume of the drops increased.
12. Silicon wafers were cleaned in hot piranha solution, which is a mixture of 70% H_2SO_4 and 30% H_2O_2 (30% solution in water). The wafer was placed in

this solution for one-half hour. Afterward, the wafer was thoroughly rinsed with and stored in distilled water. Before preparing the gradient surface, the wafer was rinsed again in running distilled water and then dried by blowing nitrogen over it.

13. We found that immersing the wafer in warm distilled water and rinsing in pure distilled water helped to remove some of the loosely adsorbed contamination from the surface. The gradient surface could be easily contaminated by atmospheric impurities. The surface remained clean, however, when kept immersed in pure distilled water.

14. Drops used to measure the advancing and receding contact angles were held stationary on the surface of the silicon wafer by the tip of the microsyringe used to form the drops. The contact angles were measured under quasistatic conditions, that is, after the cessation of the movement of the contact line. For quantitative correlation between drop velocity and surface energy gradient, the contact angles should be measured under dynamic conditions. These measurements are beyond the scope of our present study.

15. The thickness gradients of the monolayers were functions of the adsorption times and molecular weights of the silanes. We have also prepared gradient surfaces by using $Cl_3Si(CH_2)_7CH_3$. After a 5-min adsorption, nearly a close-packed monolayer (11 Å thick) was formed at the hydrophobic edge.

16. The thickness obtained by ellipsometry was an average over an area of about 3 mm^2.

17. The length (5 mm) of this gradient corresponds to what was detected by ellipsometry, which also matched the field of view of the telescope used

to observe the motion of water drops. While the drop moved beyond 5 mm from the hydrophobic edge, the drop became flat and thin in the region of weaker gradient.
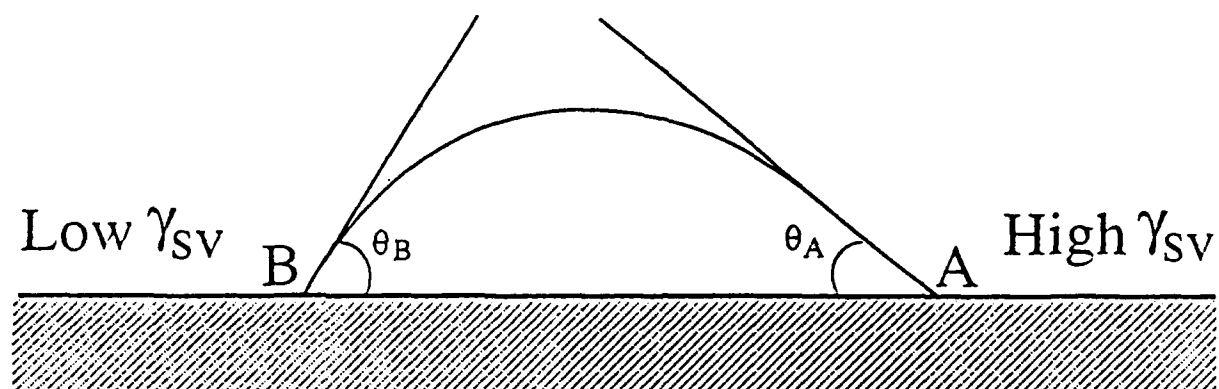
18. The Laplace length (also known as the capillary length) is $(\gamma_{LV}/\rho g)^{0.5}$, where ρ is the density of the liquid and g is the acceleration due to gravity.

19. M. K. C. acknowledges support from Dow Corning Corporation. G. M. W. acknowledges support from the Office of Naval Research and the Defense Advanced Research Projects Agency. We thank M. J. Owen (Dow Corning) for many valuable discussions.
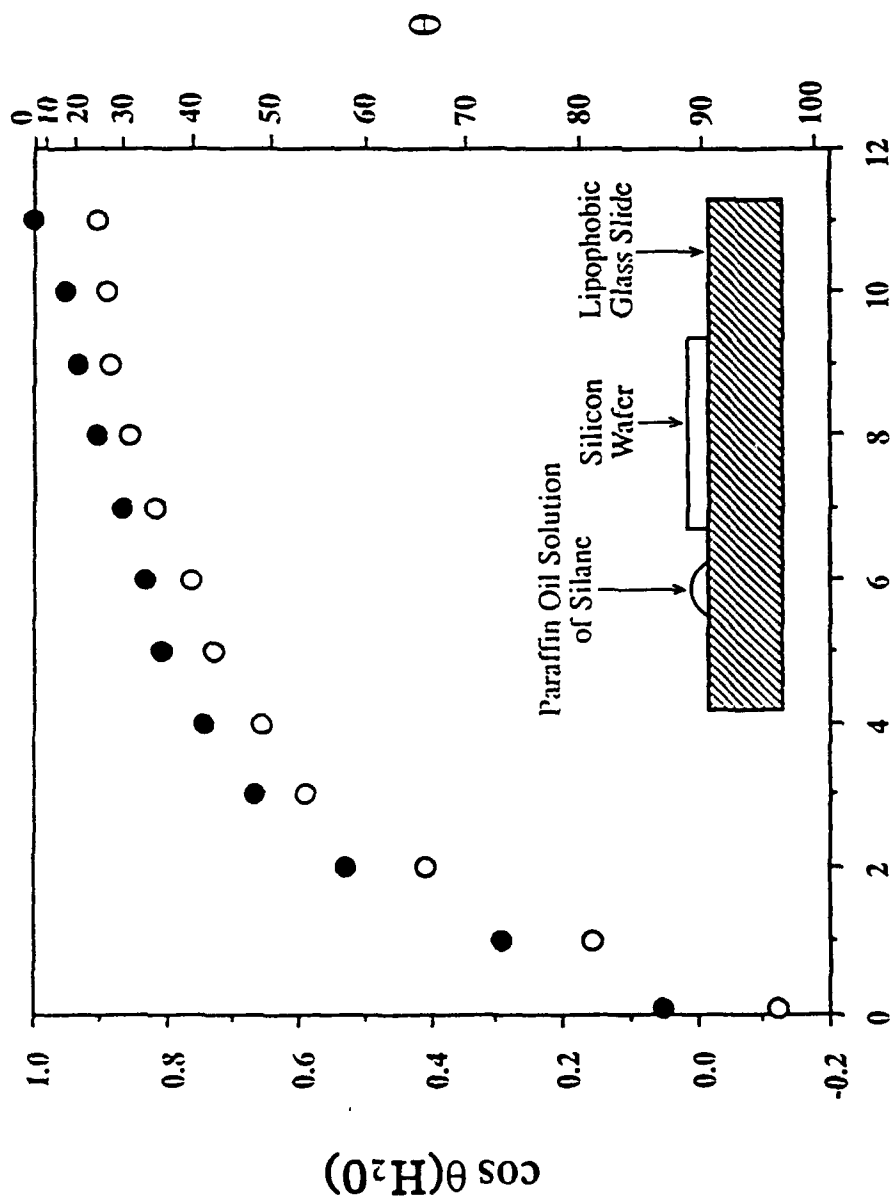
Captions

Fig. 1. Idealized diagram of a thin cross section of a liquid drop on a
gradient surface. While this diagram is useful for understanding the origin of
Young's driving force on a gradient surface, it does not state the problem
completely. Such a distorted drop shape would imply the presence of a Laplace
pressure gradient within the drop. The pressure inside the drop would equalize
and the drop would assume the shape of a spherical cap. The value of the
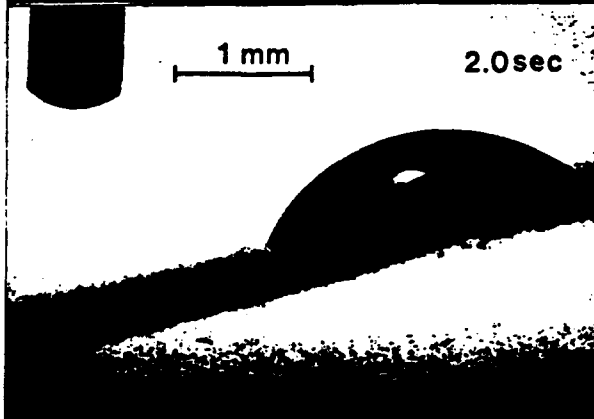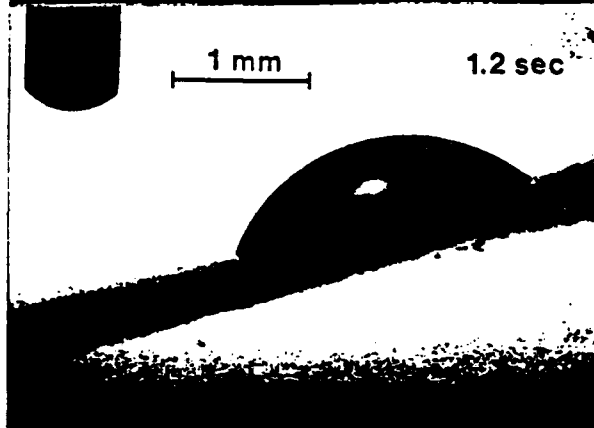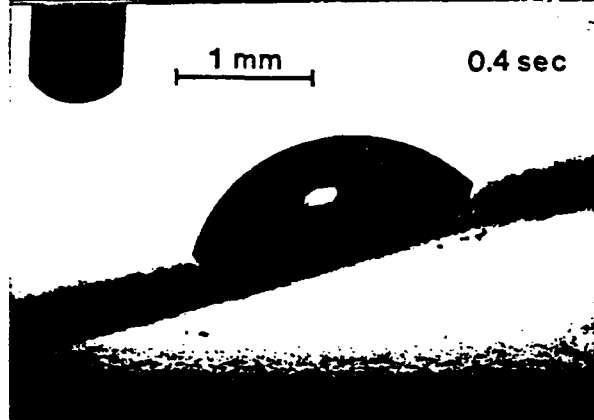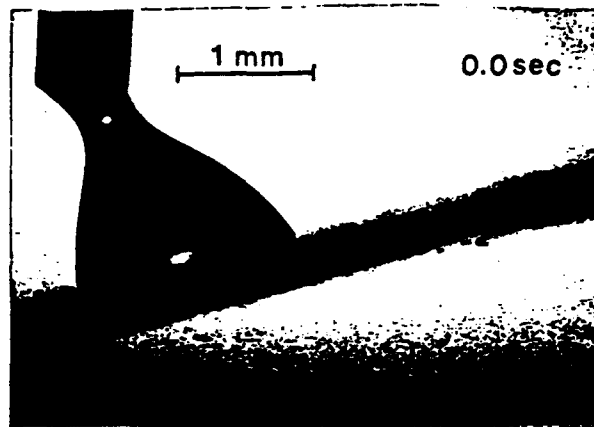dynamic contact angle would be intermediate of θ_A and θ_B.

Fig. 2. Gradient in wettability produced on a silicon wafer by 5-min exposure
to diffusing vapor of decyltrichlorosilane. The open and closed circles
represent the advancing and receding contact angles of water. In the inset,
the method used to form gradients in surface tension is illustrated
schematically. The glass slide was initially silanized with
$Cl_3Si(CH_2)_2(CF_2)CF_3$, which rendered it lipophobic. A small strip (3 mm wide) of
this slide was oxidized in plasma; this strip was used to contain the solution
of $Cl_3Si(CH_2)_9CH_3$. The solution of $Cl_3Si(CH_2)_9CH_3$ (30 μl of the silane
solution containing 75 μl of silane per gram of paraffin oil) was placed within
this strip. A clean silicon wafer (12 mm by 40 mm) was placed at a distance of
2 mm from the edge of the silane solution. The gradient surface resulted from
the diffusion of the silane in the vapor phase and subsequent reaction with the
surface SiOH groups and adsorbed water on the silicon wafer. The whole
assembly was placed inside a polystyrene petri dish and covered. The relative
humidity of the room was 40% during these experiments.

Fig. 3. Uphill motion of a drop of water on a gradient surface. The gradient surface was inclined by about 15° from the horizontal plane. The volume of the drop was about 1 μl. The moving drop was photographed using an automatic camera that exposed one frame every 0.4 s. The drop moved more rapidly on the initial part of the gradient than on the final part.

Low γ_{SV} B $\quad \theta_B$ $\qquad\qquad\qquad\qquad$ θ_A $\quad$ A $\quad$ High γ_{SV}

θ

0
10
20
30
40
50
60
70
80
90
100

12

10

8

6

4

2

0

Position (mm from Hydrophobic Edge)

cos θ (H₂0)

1.0

0.8

0.6

0.4

0.2

0.0

-0.2

$\cos\theta(H_2O)$

Lipophobic Glass Slide

Silicon Wafer

Paraffin Oil Solution of Silane

1 mm   0.0 sec

1 mm   0.4 sec

1 mm   1.2 sec

1 mm   2.0 sec

Fig. 3

ABSTRACT DISTRIBUTION LIST

Prof. Robert W. Armstrong
Department of Chemistry
University of California
405 Hilgard Avenue
Los Angeles CA 90024

Dr. Joseph Boyer
Department of Chemistry
University of New Orleans
New Orleans LA 70148

Professor Jerald S. Bradshaw
Department of Chemistry
Brigham Young University
Provo UT 84602

Prof. Ronald Breslow
Department of Chemistry
Columbia University
New York NY 10027

Dr. Duncan W. Brown
Advanced Technology Materials
520-B Danbury Road
New Milford CT 06776

Prof. Cynthia J. Burrows
Department of Chemistry
State University of New York
Stony Brook NY 11794-3400

Professor Peter Chen
Department of Chemistry
Harvard University
Cambridge MA 02138

Prof. Anthony W. Czarnik
Department of Chemistry
Ohio State University
120 West 18th Avenue
Columbus OH 43210-1173

Prof. Peter Dervan
Department of Chemistry
Calif Institute of Technology
Pasadena CA 91125

Prof. Francois N. Diederich
Department of Chemistry
University of California
405 Hilgard Avenue
Los Angeles CA 90024

Prof. Dennis A. Dougherty
Department of Chemistry
Calif Institute of Technology
Pasadena CA 91125

Prof. Kenneth M. Doxsee
Department of Chemistry
University of Oregon
Eugene OR 97403

Prof. Margaret C. Etter
Department of Chemistry
University of Minnesota
207 Pleasant Street SE
Minneapolis MN 55455

Prof. Wilmer K. Fife
Department of Chemistry
Indiana Univ/Purdue Univ
1125 East 38th Street
Indianapolis IN 46223

Prof. Samuel H. Gellman
Department of Chemistry
University of Wisconsin
Madison WI 53706

Prof. Thomas J. McCarthy
Department of Polymer Science
University of Massachusetts
701 Graduate Research Center
Amherst MA 01003

Prof. Arthur E. Martell
Department of Chemistry
Texas A&M University
College Station TX 77843-3255

Prof. William L. Mock
Department of Chemistry
University of Illinois at Chicago
Chicago IL 60680

Prof. Martin E. Newcomb
Department of Chemistry
Texas A&M University
Box 3578
College Station TX 77843-3255

Prof. Peter Schultz
Department of Chemistry
University of California
Berkeley CA 94720

Prof. Carol Venanzi
Department of Chemistry
New Jersey Inst of Technology
323 King Blvd.
Newark NJ 07102

Prof. Howard W. Whitlock
Department of Chemistry
University of Wisconsin
Madison WI 53706

Prof. Jeffrey D. Winkler
Department of Chemistry
The University of Chicago
5735 S. Ellis Avenue
Chicago IL 60637

Office of Naval Research
Chemistry Division, Code 1113
800 North Quincy Street
Arlington VA 22217-5000

Defense Technical Information
Center
Building 5, Cameron Station
Alexandria VA 22314

Dr. James S. Murday
Chemistry Division, Code 6100
Naval Research Laboratory
Washington DC 20375-5000

Dr. Robert Green, Director
Chemistry Division, Code 385
Naval Weapons Center
China Lake CA 93555-6001

Dr. Eugene C. Fischer
Code 2840
David Taylor Research Center
Annapolis MD 21402-5067

Dr. Elek Lindner
Naval Ocean Systems Center
Code 52
San Diego CA 92152-5000

Commanding Officer
Naval Weapons Support Center
Attn: Dr. Bernard E. Douda
Crane IN 47522-5050

Dr. Richard W. Drisko
Naval Civil Engineering
Laboratory
Code L52
Fort Hueneme CA 93043

Dr. Harold H. Singerman
David Taylor Research Center
Annapolis MD 21402-5067
ATTN: Code 283

Chief of Naval Research
Special Assistant for Marine
Corps Matters, Code 00MC
800 North Quincy Street
Arlington VA 22217-5000